COMBINING 1,3-CYCLOADDITION „CLICK“ REACTIONS WITH LIVING POLYMERIZATION CHEMISTRY

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The fixation of ligands onto molecules, surfaces and materials by use of reactions using a simple and unified chemistry is among the everlasting desires of chemists. The copper(I)-catalyzed azide/alkyne „click“-reaction [1] (also termed Sharpless „click“-reaction, a variation of the Huisgen 1,3-dipolar cycloaddition reaction between terminal acetylenes and azides) [2] is a recent re-discovery of a reaction fulfilling these requirements. Extremely high yields (usually above 95 %) are combined with a high tolerance of functional groups and reactions running at moderate temperatures.

In this lecture we report on the use of the azide/alkyne „click“ reaction for the fixation of ligands onto polymeric backbones for the generation of new materials with supramolecular ordering principles. [3] Important in this endeavor is the combination of living polymerization techniques with the „click“ reaction in order to achieve a broad range of functional groups to be attached onto specific positions of a polymeric chain. Two factors need to be taken into account to achieve this goal: (a) one concerns the chemical compatibility of the living polymerization mechanism (i.e.: cationic, ring opening (ROMP), radical) with the presence of the necessary azide- / alkyne moieties during the polymerization reaction and (b) the achievement of full completeness of the 1,3-dipolar cycloaddition-reaction. Three different approaches are presented to demonstrate the efficiency of the polymerization/”click“-chemistry protocols (see Scheme next page) in polymer- and surface science:
1. ROMP-„click“ methodology for the preparation of functionalized poly(oxynorbornenes) and their respective block-copolymers. [4] We have devised a strategy, which allows to conduct the 1,3-dipolar cycloaddition reaction either before or after the ROMP-polymerization process. Critical in this point is the control over the competing 1,3-dipolar cycloaddition reaction at the norbornene double-bond. A postmodification strategy, which introduces the azide/alkyne-moieties after the ROMP-process additionally leads to well defined structures with high ligand/polymer coupling yields.
2. Living polymerization/“click“-approach : The cationic polymerization process usually is not compatible with the presence of azido- or alkyne moieties. [5] Thus we have devised a synthetic strategy, where the living cationic polymerization of isobutylene can be combined with the azide/alkyne „click“ reactions. [6]
3. The azide/alkyne „click“ reaction can also be applied to surfaces in order to attach multiple functional groups with high yields. We demonstrate the versatility of this reaction by extension onto planar surfaces prepared as self assembled monolayers (SAMs) [7] and onto the surface of nanoparticles. [8]

All principles are used to generate supramolecular building blocks able to organize into well defined structures with a high level of order, in particular nanocomposites and sheet-like polymeric structures. [9] Thus this talk exemplifies the intense link between functionalization chemistry and material science using the „click“-chemistry approach.
(a) ROMP-“click” methodology

(b) Living cationic polymerization/“click” approach

(c) Surface-“click” reactions

References:


